STUDIES ON SULFURIZED LUBRICATION ADDITION AGENTS

BY
SALVATORE GEORGE GALLO
B.A., Oberlin College, 1940

AN ABSTRACT OF A THESIS
SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
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STUDIES ON SULFURIZED LUBRICATION ADDITION AGENTS

I. Studies with Radiosulfur

Introduction

Starting with the "germ-processed" oil of Wells and Southcombe[1] in 1920, which employed small quantities of long-chain fatty acids, the field of oiliness carriers has been expanded to include esters, halogenated organic derivatives, phosphoric acid esters, and sulfur compounds. The field of oxidation inhibitors has seen a similar expansion and now includes phenolic derivatives, aromatic amines, halogenated esters, sulfur compounds, and derivatives of phosphorus, arsenic, antimony, selenium, and tellurium.

The mechanism of oiliness improvement and oxidation inhibition are not very well understood in most cases, though in the case of some polar compounds, it has been fairly well established that oiliness improvement is the result of compact surface film formation, in which the polar end of the molecule is attracted to the metallic surface either by secondary valence forces or by actual compound formation. Evidence has been obtained in this laboratory[2,3,4] proving the formation of well oriented layers by some of the more polar addition agents.

However, when we consider the class of sulfurized addition agents we find a much more complex situation. The olefins used in the sulfurization process are comprised of mixtures of compounds of varying chain lengths. Moreover, the sulfurization process, in all likelihood, increases the complexity of the mixture. For this and similar reasons, it has been impossible to elucidate by means of x-rays and electron diffraction the mechanism of oxidation inhibition and oiliness improvement produced by these sulfurized compounds. The use of the radioactive tracer method suggested itself and was subsequently employed.

Experimental

The radioactive sulfur[5,6,7] was produced from CCl_4 by means of the cyclotron at Washington University in St. Louis, Mo., and was furnished in the form of barium sulfate. This was reduced to barium sulfide by means of hydrogen at elevated temperatures, converted to hydrogen sulfide and then to free sulfur. The last step was accomplished by passing the active hydrogen sulfide into aqueous I-KI solution. The purified sulfur was then introduced into the stoichiometric quantity of Conoco olefin according to the specifications of the commercial process.[8]

After carrying out the prescribed tests for completeness of reaction,[9] the radioactive blend was placed in contact with a series of bearing discs. Tests were made at 88°C and at room temperature. Counts were made by means of the Geiger-Müller counter and in every case a remarkably active, practically invisible film was formed. Active films were also found to form on glass. All these films were completely insoluble in benzene and carbon disulfide. Curves were obtained for the rate of film formation on Cleveland Graphite Triplate at 88°C and at room temperature.

Conclusions

Film formation by sulfurized addition agents seems to be quite general, having been tested on seven different bearing compositions as well as on glass. The mechanism of oxidation inhibition seems to embrace two principles, i.e., reduction of surface metal catalysis by alteration of surface character, and true inhibition in the body of the oil. The adherent organic film probably affords appreciable protection at the friction surfaces and probably is responsible for the oiliness improvement produced by these addition agents.

II. Corrosion Studies

Introduction

Soon after the entrance of the United States into World War II an acute shortage of tin was forseen by American in-

dustries. Numerous possible substitutes were sought all over the country at the request of the U. S. Department of Agriculture. It was suggested in this laboratory that the method of built-up molecular films of organic acids, lubrication addition agents, and other polar and semi-polar compounds might serve to prevent corrosion in food cans and thus release much vitally needed tin.

Experimental

A large variety of materials and techniques were employed for coating uncorroded sheet metal strips of exactly the same stock produced by a large can company. Tests were made by immersion of the treated metal in two representative foods—canned milk and fruit juices, taking all precautions to avoid innoculation of the media and comparing progress with frequent blanks.

Conclusions

Oriented multi-molecular layers[10,11] as well as films of sulfurized addition agents were not found to be sufficiently adherent and inert to prevent the corrosion of the metal. Of all the materials tried, lacquer and shellac were found to give the best protection, though these materials have already been tried commercially with only moderate success. A milk-plating technique was devised that might offer some possibilities for milk cans if a suitable plating bath can be found to produce denser deposits upon electrolysis of evaporated milk.

III. Other Instrumental Methods Applied to the Study of Oils and Sulfurized Addition Agents

Introduction

Ever since the development of sulfurized lubrication addition agents, the manufacturers have been confronted with the problem of the structure of the resulting product and the nature of the active constituent. The problem is an exceedingly difficult one when we consider the complexity of the mixture used as the starting material and the further changes that must certainly take place during the sulfurization.

The high boiling mixture does not lend itself to the ordinary methods of separation and analysis. Because of this it was deemed necessary to resort to less direct, instrumental methods.

Experimental

Among the instrumental methods employed were the mercury surface method, spectrographic and infra-red absorption methods, and electron microscopic methods. The mercury surface studies entailed a modification of the Cenco hydrophil balance for mercury surface work. Specimens for the electron microscope were prepared by spreading the oil on the water surface of the hydrophil balance, compressing the film to about 8 dynes and picking up a portion on collodion film.

Conclusions

A number of the difficulties in the mercury surface method were ironed out though others and perhaps more important ones still persist. The infra-red absorption method eliminated the mercaptan group as a possible functional group in the active constituent. The electron microscope is shown to have important possibilities for testing the efficiency of oil reclamation methods.

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